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THE THERMAL CONDUCTIVITY OF LIQUIDS UNDER
PRESSURE.

By P. W. BRIDGMAN.

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RUMFORD FUND.

(Continued from page 3 of cover.)

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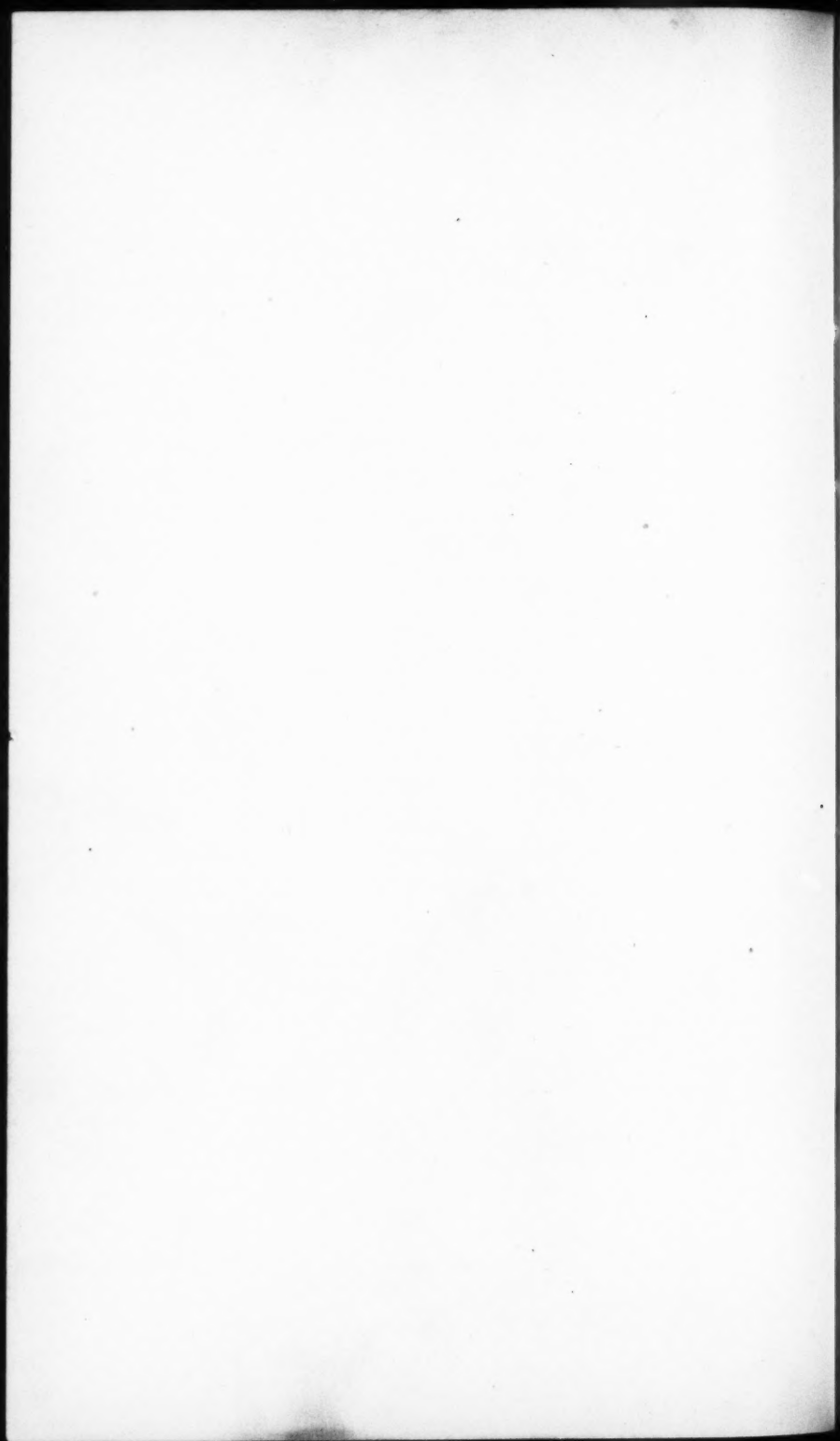
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INTRODUCTION.

In this paper I give the values of the thermal conductivity of fifteen liquids as a function of pressure between atmospheric and 12000 kg/cm² at two temperatures, 30° and 75°. The liquids chosen for investigation are for the most part those for which I have previously measured the compressibility and thermal expansion over the same range of pressure.¹ As far as I know, there have been no previous determinations of the effect of pressure on the thermal conductivity of liquids, so that the results of this paper are essentially new.

The whole field of the thermal conductivity of liquids is still largely unworked. With regard to experimental technique, there is the fundamental question of separating the part of the heat carried by radiation through the liquid from the part carried by conduction proper. This is discussed in the following. It will be seen that error from this effect may have considerably affected many previous determinations; it may well be intimately connected with the failure of many previous experimenters to agree as to the sign of the temperature coefficient of thermal conductivity. Theoretically, the thermal conductivity of liquids has been even more neglected. I have not been able to find a single attempt to deduce theoretically an expression for the thermal conductivity of a liquid, and there seems to be only one empirical expression, that of Weber.² In the following I give an expression for thermal conductivity which rests on a theoretical picture of extreme simplicity, and which, considering its simplicity, is in surprisingly good agreement with the facts.

APPARATUS AND METHOD.

The method to be employed is restricted by the requirement that the apparatus be of small enough dimensions to be contained in the pressure cylinder, and also by the requirement that the heat leak through the pressure transmitting liquid be small. This last requirement rules out a number of methods applicable at atmospheric pressure in which the heat leak from one part of the apparatus to the other is through the air and is for this reason small; such a method adapted to pressure would give a much larger heat leak because the air must be replaced by the pressure transmitting liquid.

The method adopted was one of radial flow between concentric cylinders, and is somewhat like that which I formerly used for the more poorly conducting metals.³ As far as I can find, this method has not been previously applied to measuring the thermal conductivity of liquids; it seems to offer considerable advantages over nearly all other methods, and may well be used to give more accurate results than have hitherto been attained at atmospheric pressure, as it is not at all restricted to use under pressure. The method is very rapid as well as accurate, and is particularly adapted to giving relative conductivities referred to some standard substance. Its chief disadvantage is that considerable mechanical skill is necessary in the construction of the apparatus.

Two years ago I made a preliminary attack on this problem with an apparatus somewhat like the final one, but in which the heating element and thermo-couples are both directly immersed in the liquid. This led to short circuiting effects, and furthermore, there was no adequate method of preventing the pump liquid from mixing with the liquid under measurement. With this apparatus I obtained rough values for the pressure effect on kerosene, petroleum ether, methyl alcohol, and ethyl alcohol. These results I described at the spring meeting of the National Academy of Sciences in Washington 1921, but I have published only the values of the relative conductivity of petroleum ether,⁴ which were needed as a correction term in my experiments on the thermal conductivity of metals under pressure.

The final apparatus is shown in Figure 1. The liquid to be measured, shown shaded, is contained in the annular space between two copper cylinders A and B. The outer copper cylinder B is placed inside the pressure cylinder, in which it is a fairly good fit. The pressure cylinder is filled with a liquid transmitting pressure equally to all parts of the apparatus. Thermal contact between B and the pressure

cylinder is further secured by an arrangement of flat strips of spring copper (not shown in the diagram) like those which have been described in a previous paper.⁵ The source of heat is at the axis, H, of the inner cylinder, where there is an insulated wire carrying a current of electricity. Heat flows radially from this wire through the cylinder A, the layer of liquid, the cylinder B to the pressure cylinder, and out through its steel walls to the temperature bath. The bath is rapidly stirred and maintained at a constant temperature by a regulator.

The thermal conductivity of the liquid may be calculated when the dimensions of the apparatus are known, the rate of heat input, and the difference of temperature between the outer and inner surfaces of the liquid. The formula for this is

$$k = \frac{Q}{2\pi(\theta_1 - \theta_2)} \log \frac{r_2}{r_1},$$

where k is the thermal conductivity of the liquid, Q the heat input per unit of time per unit of length along the axis, $\theta_1 - \theta_2$ the difference of temperature between the outer and inner surfaces of liquid, and r_2 and r_1 are the outer and inner radii of the layer of liquid.

Because the thermal conductivity of the copper is so much greater than that of the liquids (2500 times greater for the ordinary liquid) the temperature difference $\theta_1 - \theta_2$ may be obtained with sufficient accuracy by measuring the temperature of the metal of the cylinders A and B at points near the liquid. Practically the entire drop of temperature which drives the heat flow takes place across the layer of liquid.

The heat input Q is measured in terms of the resistance of the wire per unit length and the current. The difference of temperature is determined from the e.m.f. of

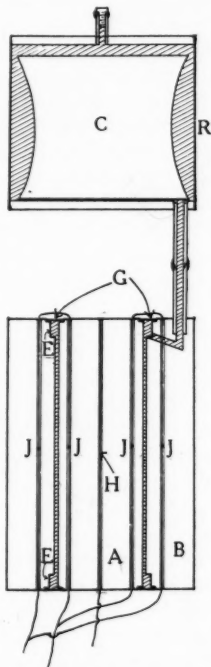


FIGURE 1. Section of apparatus for measuring thermal conductivity of liquids. The liquid is shown shaded. The upper part is a reservoir to supply the volume lost by compression. The conductivity is measured in the lower part. Heat flows radially from the heater H across the copper cylinder A across the concentric layer of liquid (shaded), across the outer copper cylinder B, and out through the surrounding pressure cylinder (not shown).

thermo-couples of copper-constantan, one of whose junctions, J, is in A and the other in B. Three of these couples were used, situated at angular intervals of 120° and connected in parallel. For convenience in drawing, two couples are shown in Figure 1. In this way the mean of three temperature differences was obtained, thus correcting for any slight geometrical irregularities.

The apparatus for measuring the heating current and the e.m.f. of the couples was the same potentiometer arrangement as that used in previous work.⁶ Its mode of construction as well as the various corrections necessary in its use have been fully described previously and need not be entered into here. All measurements could be made to considerably better than 0.1%.

The heating current was of the order of 0.3 amp.; this was maintained at the requisite constancy by an independent storage battery in series with a General Electric Co. iron-in-hydrogen ballast lamp. The resistance of the heater was such that the heat input per unit length was of the order of 0.06 watts. For the ordinary liquids, such as the alcohols, this produced between A and B a temperature difference of the order of 0.6° , giving a thermal e.m.f. of 25 micro volts.

The thermo-couples were of copper-constantan 0.006 inches (0.015 cm.) in diameter. They were composed of three pieces of wire, a central length of constantan flanked by two lengths of copper. Connections from copper to constantan were made by butt silver soldering, the entire couple after soldering being perfectly uniform in size, so that it was not possible to detect any irregularity by running the wire through the fingers. The construction of such couples has been previously described.⁷ The length of the constantan was so chosen that the two junctions copper-constantan were situated at the center of the length of the cylinder, as shown in the drawing. Situated here, any correction for end effects is a minimum. The couples were insulated with seven or eight coats of insulating enamel baked on at a temperature of about 210° . A simple calculation will show that because of the small diameter of the wire any heat leak along the constantan from the junction in A to that in B is entirely negligible.

For the heater, the high resistance alloy known as "Chromel" was used. In the earlier work a wire 0.0035 inches (0.0102 cm.) in diameter was used. This wire was originally bare, and it was insulated with enamel baked directly onto it. The mechanical strength of the insulation did not prove sufficient, however, and there were occasional short circuits. The original heater was therefore replaced in most of the work by a heating unit of 0.005 inch (0.0127 cm.) Chromel wire, double

covered with silk insulation, which was strengthened by insulating enamel baked onto it for a number of hours at a temperature low enough not to char the silk. Connection was made to the heating element at the lower end of the cylinder by a thin strip of copper, prevented from grounding to the cylinder by a thin washer of mica, and at the upper end it was grounded to the cylinder by a thin strip of German silver to which it was soldered. In this way the heater could be made accurately of the same length as the cylinder. Connections were made to the measuring apparatus through the same three terminal plug as was used in the previous work with the metals. Two of the three insulated terminals were for the thermo-couple connections, and the third was for that end of the heater which was not grounded.

Various details of the mechanical construction require comment as the successful performance depends essentially on them. In the first place, and most important, in order to secure freedom from convection currents in the liquid, particularly as the cylinders are used in a vertical position, it is necessary that the annular space between the cylinders be small. This distance was only $1/64$ inch (0.040 cm.), the outer diameter of the inner cylinder being $3/8$ inch (0.95 cm.), and the inner diameter of the outer cylinder $13/32$ inch (1.03 cm.). In the early days of thermal conductivity measurements a number of radial flow methods between concentric cylinders were used⁸ (without however using an axial source of heat as above) which have been later more or less discredited because of error due to convection. The layer of liquid used in this present apparatus is many times thinner than the thinnest used previously. Convection is further reduced by the unusually small temperature difference between the inner and the outer cylinders. The heat conveyed convectively varies, other things being equal, as the square of the temperature difference, so that it is important to keep this difference down. The thinness of the layer of liquid and the smallness of the temperature difference should together make any convection errors entirely negligible. That the performance of the apparatus in this regard was satisfactory may be seen by comparing the values of the absolute conductivity found with it with the best of previous measurements.

A further advantage of the thin layer is that the proportional part of the total heat transfer due to direct radiation through the liquid from the wall of A to that of B is thereby made a minimum. This will be discussed later.

The length of the cylinder should be as great as possible subject to the restrictions of construction and its use in the pressure cylinder.

The length actually used was 1.25 inches (3.18 cm.), 80 times as long as the thickness of the layer of liquid.

The inner cylinder was supported concentrically with the outer by rings of German silver, G, at top and bottom, 0.002 inch (0.005 cm.) thick. It is here that the difficulty of mechanical construction enters. These rings were first spun into shallow grooves turned on the two cylinders, and were then made leak tight by a very small amount of soft solder. I am indebted to the skill of Mr. David Mann for the construction of these cylinders. There is of course some heat leak from inner to outer cylinder at the two ends across the German silver rings. This is small because of the thinness of the German silver and its poor thermal conductivity. The leak was further reduced by increasing the radial separation of the two cylinders at the two ends, so that the conduction from one to the other through the liquid was decreased. By choosing the dimensions of the enlargement, E, correctly it is possible to make the decreased conductivity through the liquid exactly compensate the increased conductivity through the German silver. The dimensions were so chosen that this compensation should be exact for the average of the liquids used.

The heating unit and the thermo-couples were threaded through the cylinders in copper tubes 0.016 inch (0.041 cm.) inside diameter and 0.040 inch (0.102 cm.) outside diameter. These copper tubes were sweated into holes 0.040 inch (0.102 cm.) in diameter which were drilled lengthwise of the cylinders at the proper places, shown sufficiently to scale in the diagram. Because of the relatively low thermal conductivity of the liquids, no trouble was ever experienced arising from poor thermal contact in the sweated joints such as I had found previously with metals.

Because of the volume compression of the liquid as pressure is raised, it is necessary to provide a reservoir of the liquid outside of the space between the concentric cylinders. This was accomplished as follows. The reservoir, R, was made of a thin collapsible tube of tin 0.75 inch (1.78 cm.) in diameter, soldered at top and bottom with an easily fusible solder to end discs of brass. It was filled with liquid and connected with the annular space between the cylinders through a German silver tube. In order to cut down the volume compression as much as possible, the interior of the collapsible tube was filled with a metal core, C, of the shape shown, of such dimensions that when the tube was entirely collapsed against the core there should be a loss of volume of perhaps twice the volume compression of the liquid between the cylinders under the maximum pressure. This scheme was

entirely successful in separating the liquid to be measured from the surrounding liquid, petroleum ether or kerosene, by which pressure was transmitted from one part of the apparatus to another, and in transmitting the pressure freely to the liquid between the cylinders. The thin rings of German silver separating the inner from the outer cylinder never showed the slightest sign of deformation after a run, which, in view of their extreme thinness, is good evidence that the pressure in the liquid between the cylinders must have been very nearly the same as that in the liquid outside.

Usually it was possible to complete a set of readings on one substance, which consisted of runs at two temperatures, without rupture of the tin container, and therefore without mixing of the two liquids. At first I was afraid that there might be slight mixing, which might introduce error, and a special procedure was adopted to eliminate it. This consisted in making nearly all the readings with increasing pressure, at intervals of one thousand kilograms, instead of the usual procedure of reading at the even thousands going up and the odd thousands coming down. The purpose of the usual procedure is to eliminate error from hysteresis. By changing the procedure, any error due to a leak of the outside liquid into the reservoir and a mixing of the two liquids on releasing pressure seemed more likely to be avoided. Furthermore, because these measurements are on liquids, instead of on solids as usual, no hysteresis is to be expected, and therefore there is no reason why the procedure should not be changed. Further, check readings were always taken at 6000 and 0 after the succession of readings with increasing pressure; these check readings were found to agree with the others. The revised procedure therefore turned out after all not to be necessary. However, as the measurements had been begun in this fashion, they were continued so to the end. Even in those few cases in which the tin tube was found ruptured after a run with some escape of the inner liquid, the mixing must have been confined to the reservoir, and could not have reached to the region between the cylinders, as was proved by the consistency of the check readings.

A new tin reservoir was made for each new liquid, and connected to the copper cylinder by a soldered joint in the German silver connecting tube. The apparatus was filled in vacuum. A glass reservoir was connected to a tube at the upper end of the tin reservoir, and the whole apparatus was placed under the receiver of an air pump, and exhausted to the boiling pressure of the liquid in question. Air was then admitted, driving the liquid into the reservoir and between the copper cylinders, and then the filling was completed by several suc-

cessive boilings in vacuum, followed by admission of air. The upper end of the tube leading from the tin reservoir was then made tight by a screw soldered into place with a touch of easily fusible solder, just enough of the liquid in the upper end of the tube having been removed to make this possible.

The copper cylinders were cleaned after a run with one liquid ready for the next by several washings with ether and dryings in vacuum at room temperature or temperatures up to 130° , depending on the liquid used. There was some chemical action between the liquids and the copper, because the surface of the copper was found blackened on one occasion when an accident made necessary reassembling the cylinders, but such action must have been very slight as shown by the consistency of the check readings and the complete clearness of the liquids removed from the apparatus after a run.

CORRECTIONS.

There were the usual corrections to be made to the pressure and other electrical measurements; these need not be described in detail again here. In addition there were several peculiar to this work.

The only correction arising from the change of dimensions of the apparatus is that due to the change of length. Since the geometrical figure remains the same, the ratio of the inner and outer diameters of the layer of liquid is not altered by pressure. The change of length enters in determining the resistance of the heating element per unit length. It was assumed that the heating element retains the length of the cylinder, an assumption justified by the observation that the wire is not stretched perfectly tight, but has enough curvature to rest in spots against the sides of the containing tube. The correction for the change of length is only 0.3% at the maximum pressure of 12000 kg/cm². The resistance of the heating element changes under 12000 kg. by about 0.15%; its change with temperature between the extremes of these experiments, 30° to 75° , is about 0.7%. These corrections had been determined by previous measurements.⁹ The thermo-electric force of the couple of constantan-copper decreases under 12000 kg. by 0.77% at 30° and 0.73% at 75° . This again was determined in former work.¹⁰

The change of the thermo-electric power of the couple with temperature is a much more important factor than any of the above, and must be accurately determined if the temperature coefficient of thermal conductivity at atmospheric pressure is to be obtainable from these

measurements. In order to get this correction I made special measurements on a couple constructed of wire cut from contiguous lengths of the same spools as those from which the couples for use under pressure were made. The thermal e.m.f. of this couple was measured as a function of temperature between 20° and 95°, one of the junctions being maintained continually in ice. The measurements were checked within the limits of error by readings with both increasing and decreasing temperature. With an error at no point greater than 0.1% of any single reading, dE/dt over this range is a linear function of the temperature, and is given by the formula

$$\frac{dE}{dt} = (38.26 + .0862 t) \times 10^{-6} \text{ volts, where } t \text{ is the temperature in degrees Centigrade.}$$

This may be compared with results for other samples of constantan and copper. The figure in which we are most interested is the ratio of the thermo-electric powers at 30° and 75°. For the present material this is 1.0949. For another couple of different size wire I have previously found 1.0974,⁹ and Adams for another sample gives figures from which I calculate the ratio 1.0902.¹¹ The differences are small, but it is nevertheless evident that there are slight real differences between couples of different construction (the difference is quite as likely to be in the copper as in the constantan), and that for accurate determinations of temperature variations the particular material must be independently calibrated.

In addition to these corrections, there is a correction for heat leak from the inner to the outer cylinder due to the short circuiting action of the pressure transmitting medium in which the whole apparatus is bathed. The magnitude of this correction was determined by measuring the apparent thermal conductivity of the most poorly conducting of the liquids used in this work, namely ethyl iodide, for which the effect is greatest, first when the apparatus was mounted in the pressure cylinder without any transmitting liquid, and then when the pressure transmitting liquid was admitted. The heat leak in the first case is through the air only and may be neglected. In this first case good thermal contact between thermo-couples and heating element and the copper cylinders was ensured by a film of oil in the tubes carrying them. The correction so found was 3.5%. It is proportionally less for the better conducting liquids. This heat leak correction changes with pressure, because the effect of pressure on the thermal conducting liquid is in general different from that on the liquid under investigation.

At 30°, where it was necessary to use petroleum ether as the transmitting liquid in order to avoid mechanical deformation from increased viscosity under pressure, this correction in all except two cases increased with rising pressure. This is because the increase of thermal conductivity of petroleum ether is greater than that of the liquid being measured. It was assumed that the change in the correction was proportional to the relative change in conductivities. Thus if under 12000 kg. the increase of thermal conductivity of petroleum ether is 50% greater than that of the liquid being measured, then the heat leak at 12000 was 50% greater than at atmospheric pressure. At 75°, however, where the transmitting liquid was kerosene, the heat leak usually decreased with rising pressure. Special measurements were made on petroleum ether and kerosene to determine their conductivity under pressure.

It will be noticed that all the corrections of this method are unusually small, whether we are discussing the corrections to be applied under pressure in determining relative changes of conductivity, or the corrections to be applied at atmospheric pressure in calculating the absolute conductivities. In fact, in no case did the corrections amount to more than 4% of the effect measured. This is much smaller than for most methods at atmospheric pressure; it is gratifying that it was possible to keep the pressure corrections down to such a low value. The relations with these liquids are very much more favorable than they were for the metals previously measured, when the corrections might become as large as the effect sought.

There is another entirely different sort of correction which may well play an important part in thermal conductivity in liquids, although it has received exceedingly meager discussion; this is the effect of heat transfer by heat radiation through the liquid. There are two kinds of radiation effect to be considered. The first is the transfer of heat by radiation through the liquid from one of the walls of the containing vessel to the other, in the case above from the outer wall of the inner cylinder to the inner wall of the outer cylinder. This effect is important only in layers of liquid so thin that a large fraction of the radiation emitted from the walls is transmitted through the liquid without absorption. The thicknesses ordinarily used in thermal conductivity measurements of liquids seem to come within this range. The data do not seem to exist by which the correction can be calculated exactly. What is needed are the radiation emissivity constants of the metal of which the walls are composed at temperatures in the neighborhood of room temperatures and at those wave lengths which correspond to the

maximum emission at such temperatures. An upper limit to the correction can be obtained, however, by assuming that the walls radiate like a black body. If the two walls of the container are fairly close together, we may treat the radiation from each wall like that from an infinite plane. The net energy radiated per unit time from unit area of that wall whose temperature is $\Delta\theta$ higher than the other is given by the formula

$$u = 4K \theta^3 \Delta\theta,$$

where K is the radiation constant, and is 5.72×10^{-5} in Abs. C. G. S. units.

For 30° C. and 75° C. the formula gives the numerical values: 63.6×10^2 and 96.7×10^2 ergs, respectively, per unit temperature difference. This radiated heat is independent of the distance of separation of the walls. If now the distance between the walls is l , the amount of heat conducted from one wall to the other through the liquid in unit time is $k \frac{\Delta\theta}{l}$. The ratio of this to the heat transferred by radiation is

$$f(\theta) \frac{k}{l}.$$

With the dimensions of the apparatus used above this gives for water a ratio of 240 at 30° and 157 at 75° , or corrections for radiation of 0.42% and 0.64%. For methyl alcohol the corrections are proportionally larger, being 1.22% and 1.85% respectively.

What data there are on the emissivity of metals at low temperatures¹² would indicate that this correction, calculated as an upper limit, may be many fold too large. In consideration, therefore, of the uncertainty, I have not applied any correction at all in the following for this effect. It is to be emphasized, however, that the correction is proportional to the thickness of the layer of liquid, and that therefore the measurements here described are more advantageously situated in this regard than any previous ones. It seems to me very probable that this correction may well have a quite perceptible effect on some of the previous work; the correction is in such a direction as to make the previously calculated values larger than they should be. Since the correction increases with rising temperature, this means that too rapid an increase of conductivity with temperature may have been found previously.

The second way in which heat may be transferred by radiation is by internal radiation, from one part of the liquid to another. Every

volume element of the liquid radiates in virtue of its temperature, the radiation being greater the higher the temperature, and is a function of the liquid. Radiational equilibrium is maintained by the absorption in every volume element of a portion of the radiation from other parts of the liquid which is passing through it. If there is a temperature gradient in the liquid, there will be a net transfer of heat across any surface by radiation from the side which is hotter to the side which is cooler. Because the radiation at ordinary temperatures is not large, and because most liquids are fairly transparent, it is probable that this effect is small compared with conduction proper, and that it reaches its maximum amount only in masses of fluid so large that all the energy radiated from an element is reabsorbed before reaching the boundaries. Theoretically it does not seem certain whether there is any difference in principle between such a transfer of heat by internal radiation and the ordinary transfer by conduction. It may be that the conduction transfer is the same in kind, except that the transfer is by elastic waves from atom to atom, and that the absorption of these elastic waves is very much greater than that of the ether radiational waves, so that the effect reaches a limiting value for thicknesses of the film of liquid which are below our powers of observation. In any event, it seems that there are questions here which have not hitherto been considered with sufficient care. Experimentally it would be interesting to determine whether a liquid may not have two apparent thermal conductivities, one obtained in the limit for thin layers, and the other as the limit for thick layers. Even the possibility must be recognized that there may be no exact limit for thin layers, but that the elastic waves which convey the ordinary conduction heat are so long that the effect of their existence may be perceptible in measurable dimensions.

PROCEDURE.

The conductivity apparatus was filled with the liquid to be measured in the manner already described. The apparatus was then attached to the three terminal plug, and connections made between its terminals and the thermal junctions and heating element by soldering. The plug with the conductivity apparatus was then screwed as a single self contained piece into the pressure cylinder. Connections were made between the external leads and the leads to the measuring apparatus by soldering. The external leads were protected by a length of flexible rubber tubing pulled over them and tied to the steel cone which formed the lower part of the three terminal plug. The temperature bath of

water was then placed around the pressure cylinder, the regulator adjusted, and a sufficient time allowed to elapse for the apparatus to come to thermal equilibrium. This was shown by the vanishing of the parasitic e.m.f.'s in the thermo-couple circuit. The heating current was then switched on, and again sufficient time allowed to reach a steady state. This was now shown by the constancy of the thermo-couple readings. Regular readings were now made. These consisted of two readings of the resistance of the manganin pressure gauge on the Carey Foster bridge, and four readings each of the heating current and the thermo-couples. These four readings were made for both directions of the heating current, and for both polarities of the balancing e.m.f. In this way the effect of parasitic e.m.f.'s in the parts of the circuit external to the temperature bath were eliminated, and also the effect of any defective insulation, should there be such, between the heating circuit and the thermo-couples. All the runs retained in the final calculations were ones in which the insulation was perfect as far as could be determined. The insulation of the plug was further tested independently after every run, with the connections unsoldered, and several times the insulation of the plug was tested independently under pressure, with no leads connected. Once in a great while there was failure of the insulation, which was then repaired by re-enamelling the thermo-couples, or else installing new ones. The insulation of the heating element did not give trouble. The four readings obtained for heating current and thermal e.m.f. do not give evidence as to the freedom of the circuits inside the pressure apparatus from parasitic e.m.f.'s. This check could not be conveniently made during the course of the measurements, as has already been explained in connection with the measurements on solids. The independent test before applying the heating current should give sufficient security on this point.

After the readings of pressure, heating current, and thermal e.m.f. were completed, pressure was increased by 1000 kg., and after conditions had again become steady, the same succession of readings was repeated at the higher pressure. The time required to reach equilibrium was about ten minutes. This is very much less than in the majority of thermal conductivity experiments; it is due to the thinness of the layer of liquid, the smallness of the apparatus, and the fact that much metal was used in the construction.

The succession of readings described above was repeated at increasing intervals of 1000 kg. to a maximum pressure of 12000 kg. Check readings were then made at 6000 and zero again. This was done for

two temperatures, 30° and 75°, so that we have results for the temperature coefficient of the pressure coefficient, and also for the temperature coefficient of conductivity at atmospheric pressure, for which there are only a few previous data.

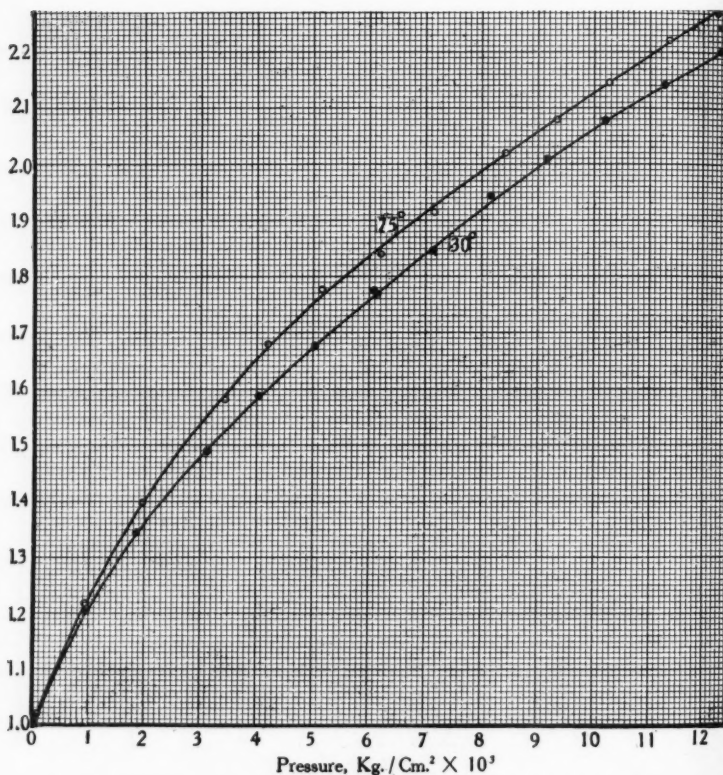


FIGURE 2. Shows the relative changes at 30° and 75° of the thermal conductivity of iso-propyl alcohol as a function of pressure. The points shown are observed points, with small corrections still to be applied.

The run at 30° was made with petroleum ether as the pressure transmitting medium. At 75° this was replaced by kerosene, because

the low boiling point of the petroleum ether, 40° , would have given inconvenience. The kerosene was introduced into the apparatus in place of the petroleum ether merely by raising the temperature at atmospheric pressure, allowing the ether to boil out, and then forcing kerosene into its place with a very slight pressure. For those liquids which boil at atmospheric pressure below 75° , the lowest pressure reading at 75° was made under a pressure of 100 kg. or so, and the results which are tabulated in the following were obtained by extrapolation to zero, the amount of the extrapolation being usually only two or three per cent.

Nearly all the points obtained lay on smooth curves within a small limit of error. In fact, the regularity of the results was very gratifying. Occasionally, however, a point was obtained which lay very widely off the curve. This was almost always due to failure of the temperature regulator of the bath to function properly. If the temperature of the bath got away from its steady value by as much as one tenth of a degree, as it did sometimes from accidental causes, a sufficient temperature gradient was set up in the leads of the three-terminal plug, which consisted of piano wire and copper, to introduce comparatively large parasitic e.m.f.'s, and so give bad points. These points were of course discarded in taking the final results, and the fact that they were found at all has nothing at all to do with the validity of the rest of the measurements.

In view of the regularity of the results it does not seem necessary to reproduce in detail the data obtained for each substance. An idea of the consistency of the results may be obtained from Figure 2, which shows the *uncorrected* relative results obtained for iso-propyl alcohol, a substance for which the results were of average regularity.

DETAILED DATA.

Most of the results for the various substances can be collected into a systematic table, in which all the substances are treated alike. In this table will be given the absolute conductivities at atmospheric pressure at 30° and 75° (extrapolated values at 75° marked with an asterisk), the relative conductivity at intervals of 1000 kg. at each of these temperatures in terms of the conductivity at atmospheric pressure as unity (the changes are smoothed so as to give regular first differences), and finally at the end of each row of pressure data the average deviation from a smooth curve of the observed points (not including in the average the points discarded as already explained because of failure of

the temperature regulator). The average deviation is given as a percentage of the maximum effect; it was obtained by adding graphically (with the dividers) all the deviations, and dividing this sum by the total number of summands and the maximum ordinate, a number usually in the neighborhood of 2.25.

In addition to the data which are of the same character for all substances and can be systematically treated in a table, there are various individual differences, which will be specifically mentioned in the following.

Choice, Source, and Purity of the Materials. In the first place, I endeavored to measure as many of those liquids as possible for which I had already determined the compressibility and other thermodynamic properties under pressure.¹ There were twelve of these liquids. Of these ten are studied here. Ethyl chloride was omitted because of the difficulty of manipulating it arising from its volatility, and phosphorus trichloride was omitted because of the difficulty of getting it pure and because of its corrosive action on metal. It was not feasible to use the same sorts of propyl and butyl alcohols in the two series of measurements. The thermodynamic data under pressure were determined for normal propyl and iso-butyl alcohols, whereas the thermal conductivity measurements of this paper were made on iso-propyl and normal butyl. The two sets of measurements are not, therefore, exactly comparable. In addition to these ten liquids, petroleum ether and kerosene were measured, particularly because their properties enter the corrections, and water, toluol, and normal pentane. The list of easily obtainable liquids which may be studied over a wide pressure range is not large, because so many freeze under pressure. Thus at 30° the usual pressure range of 12000 kg. was curtailed by freezing in the case of water, acetone, and toluol. For toluol I was able to obtain a value for the thermal conductivity of the solid (there seems to be only one other determination of the thermal conductivity of an organic liquid in the liquid and solid states¹³). It would not have been possible to undertake a systematic study of this subject with the present apparatus because of danger of mechanical rupture when pressure is applied to the solid.

The following liquids I owe to the kindness of Professor Frederick Keyes of the Mass. Institute of Technology: methyl and ethyl alcohol, sulfuric ether, carbon bisulfide, toluol, and normal pentane. These were of extreme purity, and were purified by the method described by him.¹⁴ The purity is so great that it is possible to use the freezing points as fixed points in low temperature thermometry. The liquids

were sealed into glass containers immediately after purification, and the containers were not opened until immediately before the filling of the pressure apparatus. Iso-propyl and normal butyl alcohol I owe to the kindness of Professor Brinell of Bryn Mawr, by whom they had been especially prepared and purified. These were not sealed into glass, but after preparation were left standing in the dark in glass stoppered bottles for a year or so. The acetone (from bisulfite) was obtained from the Eastman Kodak Co., as were also the iso-amyl alcohol, and the ethyl bromide and iodide. These were shipped in glass stoppered bottles, sealed with celluloid, and were perfectly colorless, except the ethyl iodide, which showed a slightly brownish tinge. I redistilled this immediately before use in a Hempel column, completely removing the color. In spite of the color, the distillation took place completely at a temperature constant within 0.1° . The water was ordinary laboratory distilled water, distilled in a tin still. Kerosene and petroleum ether were commercial articles. These are probably not entirely reproducible, but pains was taken during the experiment to use only material from the same original lots, so that there can be no error in the corrections due to chance variations of the composition of either of these liquids.

The precautions described above to ensure pure materials are probably quite superfluous for this kind of work, because the thermal conductivity of all known organic liquids (excepting water) varies over a range of only two fold, and it has been proved by Lees¹⁵ that the conductivity of a mixture may be calculated by the law of mixtures from the conductivities of the constituents.

For most of the substances only one set of runs, with a single filling of the apparatus, was made. The following substances are exceptions. A number of preliminary runs were made with methyl alcohol, with a poorly constructed preliminary apparatus, giving results which could not be retained. With the final apparatus, runs were made with two separate fillings, there having been difficulties due to leak in the pressure cylinder, and also leak from the tin reservoir. The less satisfactory of these two fillings gave results for the conductivity at atmospheric pressure differing from the more satisfactory one by 1% at 30° and 2% at 75° . Two fillings with ethyl iodide were necessary because of escape of the liquid from the tin reservoir. Check readings of the absolute conductivity at atmospheric pressure at 30° differed by 0.5%. Two complete sets of runs were made with water, not because of any difficulty, but because of the importance of the substance and in order to check the readings. The second run was made with a modi-

fied arrangement of the electrical measuring apparatus which did not allow the absolute values of the conductivity to be obtained with accuracy, but which did give accurately the relative values of the conductivity. The maximum difference between the smoothed results of these two sets of runs at any point was 0.8%, and the average arithmetical difference was 0.29%. Because of the high value of its absolute conductivity, the check afforded by the repetition is more severe in the case of water than for any of the other liquids.

It may be thought that the consistency of the results would justify one more significant figure than is given for the absolute conductivity. However this is probably not true, the absolute conductivities being limited by the accuracy of the measured dimensions of the apparatus.

Discussion of Results. The results are now given in Table I.

Before discussing the pressure effects, it will pay to consider the absolute values of the conductivities at atmospheric pressure, as this is a subject with regard to which previous measurements are considerably at variance, and the results obtained with this new apparatus should be of value from this point of view, as well as with regard to the pressure effects.

In Table II are collected for comparison my values of the absolute conductivity at atmospheric pressure at 30° and the best of previous determinations. Few of these previous determinations have been made at 30°; in the table I have indicated the temperature at which they were made. In most cases the temperature coefficient of conductivity is so small that the correction for temperature difference would be beyond the accuracy of previous work; in those cases where a temperature correction seems called for, the necessary data may be obtained from my values at 30° and 75°, assuming a linear relation between temperature and conductivity. (In the case of the data of Goldschmidt, I have placed in parentheses besides Goldschmidt's values for 0° the values which would be computed for 30°, using my value of the temperature coefficient.) The values listed in the Table are only the more recent ones, and those which apparently represent the most careful work. The discrepancies are very large, much larger than they should be for measurements on well defined substances. On the whole my agreement with Goldschmidt, the most recent as well as the most extensive of the previous work, is the best. The agreement with Lees is also good.

TABLE I.
COLLECTED RESULTS.

Liquid	Temperature	Conductivity at 0 kg.	Relative Conductivity as a Function of							
			0	1000	2000	3000	4000	5000	6000	7000
Methyl Alcohol	30°	.000505	1.000	1.201	1.342	1.458	1.557	1.645	1.724	1.797
	75°	493*	1.000	1.212	1.365	1.492	1.601	1.698	1.785	1.865
Ethyl Alcohol	30°	.000430	1.000	1.221	1.363	1.477	1.574	1.663	1.744	1.820
	75°	416*	1.000	1.233	1.400	1.535	1.650	1.752	1.845	1.930
Isopropyl Alcohol	30°	.000367	1.000	1.205	1.352	1.469	1.570	1.660	1.743	1.821
	75°	363	1.000	1.230	1.399	1.530	1.638	1.730	1.812	1.890
Normal Butyl Alcohol	30°	.000400	1.000	1.181	1.307	1.408	1.495	1.575	1.648	1.716
	75°	391	1.000	1.218	1.358	1.465	1.559	1.643	1.720	1.791
Isoamyl Alcohol	30°	.000354	1.000	1.184	1.320	1.430	1.524	1.608	1.686	1.759
	75°	348	1.000	1.207	1.348	1.460	1.557	1.645	1.724	1.797
Ether	30°	.000329	1.000	1.305	1.509	1.667	1.800	1.911	2.009	2.097
	75°	322*	1.000	1.313	1.518	1.677	1.814	1.935	2.043	2.142
Acetone	30°	.000429	1.000	1.184	1.315	1.421	1.511	1.589	1.659	1.725
	75°	403*	1.000	1.181	1.325	1.447	1.554	1.650	1.738	1.817
Carbon Bisulfide	30°	.000382	1.000	1.174	1.310	1.419	1.512	1.592	1.663	1.726
	75°	362*	1.000	1.208	1.366	1.497	1.607	1.705	1.789	1.866
Ethyl Bromide	30°	.000286	1.000	1.193	1.327	1.431	1.517	1.592	1.657	1.715
	75°	273*	1.000	1.230	1.390	1.510	1.609	1.695	1.772	1.843
Ethyl Iodide	30°	.000265	1.000	1.125	1.232	1.319	1.394	1.456	1.509	1.553
	75°	261	1.000	1.148	1.265	1.362	1.442	1.510	1.570	1.622
Water	30°	.00144	1.000	1.058	1.113	1.163	1.210	1.253	1.293	1.332
	75°	154	1.000	1.065	1.123	1.176	1.225	1.268	1.308	1.345
Tolnol	30°	.000364	1.000	1.159	1.286	1.387	1.470	1.541	1.604	1.661
	75°	339	1.000	1.210	1.355	1.473	1.573	1.660	1.738	1.808
Normal Pentane	30°	.000322	1.000	1.281	1.483	1.644	1.777	1.889	1.987	2.077
	75°	307*	1.000	1.319	1.534	1.707	1.855	1.990	2.112	2.226
Petroleum Ether	30°	.000312	1.000	1.266	1.460	1.618	1.752	1.868	1.970	2.062
	75°	302*	1.000	1.268	1.466	1.635	1.780	1.909	2.026	2.132
Kerosene	30°	.000357								
	75°	333	1.000	1.185	1.314	1.417	1.502	1.580	1.654	1.724

* Extrapolated, see page 155.

† Tolnol freezes at 9900 kg/cm² at 30°. The figure at 11000 is for the solid.

rity	Relati			
	0	1000	2000	3000
5	1.000	1.201	1.342	1.458
3*	1.000	1.212	1.365	1.492
0	1.000	1.221	1.363	1.477
6*	1.000	1.233	1.400	1.535
7	1.000	1.205	1.352	1.469
8	1.000	1.230	1.399	1.530
9	1.000	1.181	1.307	1.408
0	1.000	1.218	1.358	1.465
1	1.000	1.184	1.320	1.430
2	1.000	1.207	1.348	1.460
3	1.000	1.305	1.509	1.667
4	1.000	1.313	1.518	1.677
5	1.000	1.184	1.315	1.421
6	1.000	1.181	1.325	1.447
7	1.000	1.174	1.310	1.419
8	1.000	1.208	1.366	1.497
9	1.000	1.193	1.327	1.431
0	1.000	1.230	1.390	1.510
1	1.000	1.125	1.232	1.319
2	1.000	1.148	1.265	1.362
3	1.000	1.058	1.113	1.163
4	1.000	1.065	1.123	1.176
5	1.000	1.159	1.286	1.387
6	1.000	1.210	1.355	1.473
7	1.000	1.281	1.483	1.644
8	1.000	1.319	1.534	1.707
9	1.000	1.266	1.460	1.618
0	1.000	1.268	1.466	1.635
1	1.000	1.185	1.314	1.417

Figure at 11000 is for the solid.

TABLE I.
COLLECTED RESULTS.

Relative Conductivity as a Function of Pressure in kg/cm ²										Percentage Deviation from Smooth Curve
	4000	5000	6000	7000	8000	9000	10000	11000	12000	
8	1.557	1.645	1.724	1.797	1.864	1.927	1.986	2.043	2.097	.09
2	1.601	1.698	1.785	1.865	1.939	2.007	2.072	2.133	2.191	.27
7	1.574	1.663	1.744	1.820	1.888	1.954	2.014	2.070	2.122	.14
5	1.650	1.752	1.845	1.930	2.007	2.083	2.152	2.217	2.278	.23
9	1.570	1.660	1.743	1.821	1.894	1.963	2.028	2.091	2.150	.08
0	1.638	1.730	1.812	1.890	1.962	2.030	2.093	2.154	2.211	.21
8	1.495	1.575	1.648	1.716	1.780	1.842	1.900	1.955	2.008	.15
5	1.559	1.643	1.720	1.791	1.859	1.923	1.985	2.043	2.099	.18
0	1.524	1.608	1.686	1.759	1.828	1.893	1.955	2.013	2.069	.31
0	1.557	1.645	1.724	1.797	1.868	1.934	1.998	2.063	2.126	.25
7	1.800	1.911	2.009	2.097	2.177	2.251	2.322	2.388	2.451	.25
7	1.814	1.935	2.043	2.142	2.231	2.316	2.394	2.469	2.537	.21
1	1.511	1.589	1.659	1.725	1.786	1.864	1.900	Freezes		.08
7	1.554	1.650	1.738	1.817	1.891	1.960	2.024	2.083	2.137	.23
9	1.512	1.592	1.663	1.726	1.783	1.834	1.880	1.923	1.962	.06
7	1.607	1.705	1.789	1.866	1.935	1.998	2.054	2.107	2.154	.14
1	1.517	1.592	1.657	1.715	1.768	1.815	1.858	1.895	1.928	.12
0	1.609	1.695	1.772	1.843	1.907	1.944	2.022	2.073	2.121	.12
9	1.394	1.456	1.509	1.553	1.592	1.628	1.662	1.694	1.724	.09
2	1.442	1.510	1.570	1.622	1.671	1.715	1.757	1.799	1.837	.15
3	1.210	1.253	1.293	1.332	1.366	1.398	1.428	1.456	Freezes 1.506	.14
3	1.225	1.268	1.308	1.345	1.379	1.412	1.445	1.476		.09
7	1.470	1.541	1.604	1.661	1.716	1.768		(2.394†)		.11
3	1.573	1.660	1.738	1.808	1.872	1.932	1.987	2.039	2.089	.16
4	1.777	1.889	1.987	2.077	2.163	2.245	2.325	2.404	2.481	.14
7	1.855	1.990	2.112	2.226	2.335	2.440	2.543	2.642	2.740	.08
3	1.752	1.868	1.970	2.062	2.143	2.215	2.279	2.333	2.379	.25
5	1.780	1.909	2.026	2.132	2.232	2.324	2.409	2.488	2.561	.26
7	1.502	1.580	1.654	1.724	1.792	1.859	1.925	1.990	2.054	.24

TABLE I
Collected Results

Isotope	Temperature (°C)	Conductivity at 0.25 mole/l.	Relative Conductivity					
			1000	2000	3000	4000	5000	
Hydrogen	100	0.00002	1.000	1.001	1.002	1.003	1.004	
	150	0.00002	1.000	1.001	1.002	1.003	1.004	
Deuterium	100	0.00002	1.000	1.001	1.002	1.003	1.004	
	150	0.00002	1.000	1.001	1.002	1.003	1.004	
Helium	100	0.00002	1.000	1.001	1.002	1.003	1.004	
	150	0.00002	1.000	1.001	1.002	1.003	1.004	
Neon	100	0.00002	1.000	1.001	1.002	1.003	1.004	
	150	0.00002	1.000	1.001	1.002	1.003	1.004	
Argon	100	0.00002	1.000	1.001	1.002	1.003	1.004	
	150	0.00002	1.000	1.001	1.002	1.003	1.004	
Krypton	100	0.00002	1.000	1.001	1.002	1.003	1.004	
	150	0.00002	1.000	1.001	1.002	1.003	1.004	
Xenon	100	0.00002	1.000	1.001	1.002	1.003	1.004	
	150	0.00002	1.000	1.001	1.002	1.003	1.004	
Radon	100	0.00002	1.000	1.001	1.002	1.003	1.004	
	150	0.00002	1.000	1.001	1.002	1.003	1.004	

* Extrapolated, see page 125.
† Values between 1000 and 2000 are for the whole.

TABLE II.

COMPARISON OF THERMAL CONDUCTIVITY AT ATMOSPHERIC PRESSURE BY
DIFFERENT OBSERVERS.

Liquid	Goldschmidt ¹⁶ 0°	Lees ¹⁵ 25°	Weber ² 1880 0°	Weber ² 1885 9°-15°	Graetz ¹⁷	DeHeen ¹⁸	Chree ¹⁹ 19°	Bridgman 30°
Methyl Alcohol	.000524 (522)	48.		495		393	58	505
Ethyl Alcohol	.000446 (436)	43	49	423	55	347	59	430
Isopropyl Alcohol	.000368 (366)			373(?)				367
Isoamyl Alcohol				33		265		354
Ether	.000338 (333)		41	303	38			329
Acetone	.000423 (407)							429
Carbon Bisulfide	.000388 (375)		42		27		54	382
Ethyl Bromide				247				286
Ethyl Iodide				222				265
Water	.00150 (157)	136	124	136	157		136	144
Tolnol	.000349 (333)			307				364

Probably the most careful work on thermal conductivity of liquids has been by Milner and Chattock²⁰ and by Jakob²¹; both are, however, confined to the single liquid water. In the paper of Jakob will be found a careful critical survey of previous work, in which the various sources of error are pointed out. These possible errors seem so large that none of the work before Jakob can be relied on to give even the sign of the temperature coefficient of conductivity. (Milner and Chattock did not attempt to get the coefficient of water with any accuracy, but from the results of readings differing in mean temperature by only one degree they estimated that the coefficient would be found to be positive.) It is gratifying to note that these best previous values for water agree closely with that found above. I find at 30° 0.00144, Jakob gives 0.001444, and the value 0.001433 given by Milner and Chattock for 20° corrects to 0.001455 at 30°, using my value of the temperature coefficient. We may probably take at 30° as the most probably correct value to three significant figures 0.00144.

Temperature Coefficient of Conductivity. I have already stated that the discussion of Jakob makes probable that none of the work before his can be relied on to give the sign of the temperature coefficient. The previous experiments which make the most serious pretensions in this regard are of Lees¹⁵ and of Goldschmidt.¹⁶ Lees finds the temperature coefficient of four liquids, water, glycerine, methyl and ethyl alcohol, to be negative, and fairly large, varying from 0.3 to 0.6% per degree. Goldschmidt finds the temperature coefficient of those few liquids which he measured (he did not measure water) to be always negative, and something of the order of 0.2% per degree.

I find the temperature coefficient of all the liquids measured here with the exception of water to be negative, but considerably smaller than either Lees or Goldschmidt. It varies from -0.02% per degree for iso-propyl alcohol to -0.15% for toluol and kerosene, these coefficients being in terms of the conductivity at 30°. For water I find 0.22% per degree in terms of the conductivity at 30°. The only previous value seriously to be compared with this is 0.28% at 30° of Jakob. The agreement is much closer than that of any previous work, and perhaps one should be satisfied, but nevertheless it would seem that the agreement should be closer when the self consistency of either piece of work by itself is considered, or the estimates of either of us as to the probable error of our results. The difference is in the direction of the radiation effect, discussed above.

Pressure Effects. In general characteristics the effect of pressure is the same on all the liquids tried. The thermal conductivity increases

under pressure by an amount for 12000 kg/cm² which varies from 1.5 fold for water to 2.7 fold for normal pentane. In general the effect is greater for those substances with the lower boiling or freezing points (these are also the more compressible substances). The effect is not at all proportional to pressure, but at high pressures a given increment of pressure produces a much smaller effect, both absolutely and relatively, than at lower pressures. It may be seen from the results in Table I that the second 6000 kg. produces an effect which is in general about half that of the first 6000 kg.

The figures given in the table for kerosene smooth out an effect whose existence seems pretty certain, but which could not be established quantitatively with accuracy. Between 6000 and 12000 kg. there seems to be a slight reversal in the direction of curvature of the curve giving conductivity as a function of pressure; this effect is roughly large enough to depress the ratio at 9000 kg. to 0.020 less than the value given. Similar effects have been found previously for the volume of kerosene as a function of pressure and temperature. The explanation is doubtless to be found in the gradual freezing out over a range of pressure of the various pure components of which kerosene is composed.

The relative effect of pressure is greater at 75° than at 30° by something of the order of 5 or 10%. This change with temperature is so large that at the upper end of the pressure range the temperature coefficient of conductivity is reversed, and all the liquids are more conducting at the higher temperature at high pressures. The pressure at which this reversal takes place varies somewhat with the liquid, but as a rough average it is about 3000 kg/cm². This reversal by pressure of a temperature relation is not the first instance, but I have previously found ¹ that at high pressures the thermal expansion of all these liquids is greater at low temperatures rather than at high temperatures, which is the normal behavior at atmospheric pressure. It may be significant that the pressure of reversal of this effect was also roughly 3000 kg/cm².

The conductivity of solid toluol at 11000 kg. is about 28% greater than that for the liquid extrapolated to the same pressure. We would in general expect the solid to have the greater conductivity because its specific volume is less than that of the liquid and the velocity of elastic waves in it is greater, and this is also what has been found by Barus ¹³ for the only other organic substance which I know of which has been measured in the solid and the liquid. Barus found at atmospheric pressure that the conductivity of solid thymol was greater than that of the liquid. The physical constants of neither toluol or thymol in the solid state are known, so that we cannot go farther and compare the

difference between the solid and the liquid with the difference to be expected in terms of the theoretical picture to be given in the next section.

THEORETICAL CONSIDERATIONS.

The thermal conductivity of liquids is a subject which has received very little theoretical attention. It has been recognized that the mechanism of conduction in a liquid must be different from that in a gas. In the gas there is an intimate connection between thermal conduction and viscosity; each is connected with the length of free molecular flight, conductivity being concerned with the transfer of energy and viscosity with the transfer of momentum. The relation between these is exhibited by the elementary formula

$$\kappa = \eta C,$$

η being viscosity and C specific heat. That there is no such relation for liquids may be shown in the first place by substituting numerical values into this formula; the thermal conductivity will be found to be of the order of ten fold too small. The failure of a relation between conductivity and viscosity has also been shown by experiments²² in which the viscosity of a solution of gelatine in water has been varied by a factor of many fold, with only slight changes in the thermal conductivity. The same is suggested by the pressure experiments above; there is very good evidence that the change of viscosity of at least some of the liquids measured above is many fold greater than the change found in the thermal conductivity.

So far as I know, there is only one empirical relation connecting the thermal conductivity of liquids with their other properties. This is the formula of Weber,² first given as $\kappa/\rho c = \text{Const}$, and later modified to

$$\frac{\kappa}{\rho c} \left(\frac{m}{\rho} \right)^{\frac{1}{3}} = \text{Const.}$$

Here ρ is the density of the liquid, c its specific heat, and m its molecular weight. The factor $\left(\frac{m}{\rho} \right)^{\frac{1}{3}}$, by which the modified formula

differs from the original one, is seen to be proportional to the mean distance of separation between the centers of the molecules. Weber's own data indicated a surprising constancy of the modified expression, the average for most liquids being in the neighborhood of 0.210, with

extreme variations from 0.271 for sulfuric acid to 0.186 for iso-butyl iodide. Later discussion, however, has disclosed considerably greater variations than supposed by Weber. Van Aubel²³ has shown that the constant varies with temperature considerably for a single substance, and that recent determinations of thermal conductivity by Lees,¹⁵ which presumably are more accurate, do not fit as well. It seems probable that the relation discovered by Weber has no particular absolute significance. He gave no way of calculating the constant, which turns out to have the dimensions of $M^{-\frac{1}{3}} L^3 T \theta^2$. No simple relation between a constant of these dimensions and any of the fundamental constants of nature has suggested itself to me. It is to be expected *a priori* that it would not be difficult to discover relations like those of Weber, because the properties of ordinary organic liquids vary through only a comparatively small range.

In the course of speculations on the significance of the data above, I have come across an expression for thermal conductivity which I have not found mentioned before, and which is different from that of Weber in that it enables us to calculate completely the thermal conductivity, leaving no empirical constant unaccounted for. The relation is

$$\kappa = 2\alpha v/\delta^2,$$

where α is the gas constant, v the velocity of sound in the liquid, and δ the mean distance of separation of centers of molecules, assuming an arrangement cubical on the average, and calculating δ by the formula $\delta = \left(\frac{m}{\rho}\right)^{\frac{1}{3}}$, where m is the absolute weight in grams of one molecule of the liquid.

In Table III are shown the computed and observed values of thermal conductivity for those substances for which the necessary data have been procured. The velocity of sound has been directly determined for only a few liquids. In order to treat all liquids consistently, I give in the table the velocity calculated from my values for the compressibility. The compressibility that enters the formula for velocity is the adiabatic compressibility. This is given in terms of the isothermal compressibility, the thermal expansion, the specific heat, and the absolute temperature by the formula

$$\left(\frac{\partial v}{\partial p}\right)_s = \left(\frac{\partial v}{\partial p}\right)_\tau + \frac{\tau}{c_p} \left(\frac{\partial v}{\partial \tau}\right)_p.$$

Here the second term is a small correction term, and the values of thermal expansion and specific heat used in the computation of it were

TABLE III.

COMPARISON OF COMPUTED AND OBSERVED THERMAL CONDUCTIVITIES AT 30°.

Liquid	Velocity of Sound cm/sec.	δ^{-2} cm ⁻²	Thermal Conductivity Abs. C. G. S. Units	
			Computed	Observed
Methyl Alcohol	1.13×10^5	6.00×10^{14}	27.4×10^3	21.1×10^3
Ethyl Alcohol	1.14	4.74	21.8	18.0
Propyl * Alcohol	1.24	3.94	19.7	15.4
Butyl * Alcohol	1.05	3.49	14.9	16.7
Iso-amyl Alcohol	1.24	3.13	15.7	14.8
Ether	.92	3.19	11.9	13.7
Acetone	1.14	4.00	18.5	17.9
Carbon Bisulfide	1.18	4.61	21.9	15.9
Ethyl Bromide	.90	3.97	14.5	12.0
Ethyl Iodide	.78	3.81	12.1	11.1
Water	1.50	10.4	63.0	60.1

* Computed for normal propyl and iso-butyl alcohols, observed for iso-propyl and normal butyl.

taken from tables of constants. The calculated velocity agrees with the directly determined velocity within a couple of per cent where the comparison is possible.

In view of the simplicity of the relation, the agreement between experiment and calculation shown in Table III is surprising. It is particularly surprising that the high conductivity of water is reproduced so closely. The high conductivity of water therefore does not appear to be due in any special way to the molecular peculiarities of water (two or more molecular species) but is directly referable to its low compressibility and the fact that the centers of the molecules are closer together than in the average liquid.

The physical picture in terms of which this expression for thermal conductivity may be obtained is as follows. Imagine the molecules in simple cubical array, the distance between molecular centers being δ . Let there be in the liquid a temperature gradient $d\theta/dx$. The energy of a molecule is $2\alpha\theta$ (half potential and half kinetic), where α is the gas constant, 2.02×10^{-16} , and θ is the absolute temperature. The difference of energy between neighboring molecules in the direction of the temperature gradient is $2\alpha\delta d\theta/dx$. This energy difference is to be conceived as handed down a row of molecules with the velocity of sound. The total energy transferred across a fixed point of any row of molecules per unit time is the product of the energy difference and the number of such energy steps contained in a row v cms. long, or $2\alpha\delta (d\theta/dx) v/\delta$. The total transfer across unit cross section is the product of the transfer across a single row and the number of rows, or $2\alpha v (d\theta/dx) \delta^{-2}$. But by the definition of thermal conductivity this transfer is also $\kappa d\theta/dx$. Whence, identifying coefficients, we have for the thermal conductivity

$$\kappa = 2\alpha v \delta^{-2}.$$

I gave this formula at the spring meeting of the American Physical Society in Washington 1923, but did not publish it as part of my abstract²⁴ because I discovered it too late.

Not only does this very simple expression give approximately the absolute magnitude of the thermal conductivity, but it also accounts for the sign, although not the numerical magnitude, of the temperature coefficient of conductivity. Thus it will be found that for the ordinary organic liquid both v and δ^{-2} decrease with rising temperature, giving a conductivity decreasing with rising temperature, as found experimentally. For water, on the other hand, v increases with rising temperature (both the isothermal compressibility and the thermal expansion of water changing abnormally with temperature) at a rate

more than sufficient to compensate for the decrease of δ^{-2} , so that the net effect is an increase of conductivity, again agreeing with experiment.

In view of the success of this simple expression at atmospheric pressure, it was a surprise to me to find that it does not account at all well for the phenomena under pressure. It does, of course, give the correct sign for the pressure effect, for both v and δ^{-2} increase with pressure, so that an increase in conductivity is to be looked for. But the change given by the formula is greater than that found to be actually the case. The velocity of sound is the factor which changes most with pressure. I have already found that the ratio of the compressibility at 12000 kg. to that at atmospheric pressure for the normal organic liquid is of the order of 1 to 15. Combined with the change of density this results in a change of velocity of sound by a factor usually between 3 and 4. Combined with the factor δ^{-2} this demands a change in thermal conductivity at 12000 kg. of between three and four fold, whereas we have seen the experimental value is at most 2.7, and for the majority of liquids is in the neighborhood of 2. The computed change of conductivity with pressure for water agrees no better with experiment than it does for other liquids.

The conclusion is, therefore, that pressure produces some change in the structure of the liquid not taken account of in the simple picture above. It is not difficult to imagine what the nature of this effect may be. We have supposed the molecules to stand in more or less coherent columns or rows, so that the energy of thermal vibration may be handed on from one molecule to the next without hindrance or delay. The formation of these coherent rows we may suppose to take place naturally under the free play of molecular forces when there is no external compulsion. One is reminded of the way in which the molecules in the surface film of a liquid are known to align themselves into rows. But when external compulsion is applied, as by the application of external pressure, the simple columnar arrangement is violated, the transfer of energy from molecule to molecule down a coherent row is interfered with, and the thermal conductivity decreases.

We may with some plausibility find support for this point of view in the reversal of the temperature coefficient of conductivity at high pressures. With increasing violence of temperature agitation the molecules are brought into closer contact during part of their vibrations, and so part of that ease of transmission of thermal energy is restored which was destroyed by the unnatural configuration forced by pressure.

A corollary of this is the suggestion that an increase of external pressure is not like in all respects the so-called internal pressure due to molecular attractions.

This simple picture of the mechanism of thermal conductivity is apparently applicable only to electrically non-conducting liquids. The thermal conductivity of rock salt calculated in this way is only one quarter of the actual conductivity, and for iron it is only 1/22 of that part of the total conductivity which may be ascribed to the action of the atoms (one third of the total conductivity). For the case of liquids, our picture is essentially one in which the free path for thermal transfer is the distances between molecular centers. The fact that the thermal conductivity of solids is greater than given by this expression means that for solids the free path for thermal transfer (or the extinction distance of an elastic wave) must be much greater than the distance between centers. Of course this has been known to be the case on other grounds. In fact, the formula given above may be shown to be the same, except for the numerical coefficient, as a formula given by Debye²⁵ for the conductivity of a solid, provided we assume that Debye's quantities take the proper values in a liquid. Debye's expression for the conductivity of a solid is $\kappa = ql\rho c/4$ where q is the velocity of a distortional wave, l is the mean free path of this wave defined as the distance within which the energy of the wave drops to $1/e$ of its initial value, ρ is the density of the solid, and c its specific heat. Now let us, in accordance with the suggestion above, put l equal to δ , the distance between molecular centers. For the thermal energy of unit volume we have $\rho c = 2\alpha N = 2\alpha\delta^{-3}$. Also put $q = v$. Substituting these values in Debye's expression gives $\kappa = \alpha v\delta^{-2}/2$, agreeing with my expression except for the coefficient 1/2 instead of 2. In Debye's application of the expression to solids, the calculation of l , the mean free path of the elastic wave, is a complicated matter, and finally an expression is obtained involving the compressibility, natural frequency of vibration of the molecules, the gas constant, and the absolute temperature.

A somewhat closer connection with experiment than that given by the formula above is obtained if we set the variation of thermal conductivity with pressure merely proportional to the velocity of sound, instead of to the product of the velocity and δ^{-2} . In a paper read at the Spring meeting of the National Academy of Sciences in Washington 1921, but never published, even in abstract, I called attention to the parallelism between the change in thermal conductivity with pressure and the velocity of sound, and expressed the opinion that the

most important single factor determining the thermal conductivity of a liquid was the velocity of sound.

SUMMARY.

An apparatus is described for measuring the thermal conductivity of liquids both at atmospheric pressure and high pressures; the method uses the radial flow of heat across a thin layer of liquid contained between two concentric metal cylinders. The importance of eliminating the effect of radiation through the liquid from one wall to the other in all methods of measuring conductivity of liquids is emphasized; the effect may be minimized by making the layer thin. The method is applied to the measurement of fifteen liquids over a pressure range of 12000 kg/cm² at 30° and 75°. At atmospheric pressure the thermal conductivity of all the liquids except water decreases with rising temperature. Under pressure the conductivity increases by an amount varying from 1.5 to 2.7 fold for the entire pressure range. The effect is greatest for the most compressible liquids, and is least for water. The effect is far from linear with pressure, but the initial rate of increase of conductivity with pressure is several fold greater than the rate at 12000 kg. At pressures above roughly 3000 kg. the temperature coefficient reverses sign, so that all of these liquids are more conducting at high pressure at the higher temperatures. A simple theoretical formula for thermal conductivity of liquids has been obtained, in which the difference of temperature energy in a liquid in which there is a temperature gradient is represented as travelling through the liquid with the velocity of sound.

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